

FURTHER EVIDENCE ON THE MECHANISM OF THE CO₂ CARBON GASIFICATION CATALYZED BY CALCIUM: TPD AFTER ¹³CO₂ CHEMISORPTION

Cazorla-Amorós, D., Linares-Solano, A., Salinas-Martínez de Lecea, C.
Departamento de Química Inorgánica e Ingeniería Química
Universidad de Alicante. Alicante, Spain.

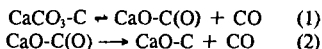
Meijer, R. and Kapteijn, F.
Department of Chemical Engineering
University of Amsterdam. The Netherlands.

Keywords: Calcium catalyst, reaction mechanism

INTRODUCTION

Previous studies [1-7] have analyzed the use of the CO₂ chemisorption on the field of the carbon-gas reactions catalyzed by calcium. The results clearly show that this technique allows to understand its catalytic activity and to gain insight into the mechanism of the reaction. Important aspects of these studies are: 1) The chemisorption of CO₂ at 573 K (5-30 min) on carbons containing calcium is restricted to the surface of the CaO particles and therefore, can be used to determine the area (and dispersion) of the catalyst particles [1, 2, 3]. 2) Temperature programmed desorptions (TPD) of calcium-carbon samples after CO₂ chemisorption give information about the calcium-carbon contact, which is responsible for the catalytic activity [4, 5]. 3) Quantification of such contact provides the number of catalytic active sites (CAS) of the catalyst, which is used to normalize the CO₂ and steam reactivities of samples with different calcium loading or with different calcium sintering degrees, and to obtain kinetic parameters of interest with respect to the mechanism of the carbon-gas reaction catalyzed by calcium [6, 7].

Information about the mechanism of the reaction have been deduced from TPD of calcium-carbon samples previously contacted with CO₂ using the following reasonings: i) During the increase in temperature in a TPD run, a redistribution of the CO₂ is produced among the CaO particles. ii) The CO₂ diffuses from the external surface to the calcium-carbon contact yielding to the formation of CaCO₃-C species. iii) The decomposition of these species, which is produced at a higher temperature, takes place through the catalyst-carbon contact, by means of a two steps gasification mechanism [5, 7]:



Accordingly to this mechanism, two types of CO should be evident; one coming from CaCO₃ and the other from the oxidized carbon atom. In other words, the reactive CO₂ molecule (*CO₂) which proceeds from CaCO₃ through its contact with the carbon should give rise to two types of CO. Two types of CO have also been distinguished recently from TPD experiments in the case of potassium [8].

From the above mentioned studies -CO₂ chemisorption and TPD- it was not possible to distinguish these two types of CO because, under the experimental conditions used, they appeared very close. Changing the experimental conditions, as it has been done recently with TPD under vacuum [9], or using isotopically labelled molecules, as done in this paper and in a previous one [10], the two steps of the mechanism of the carbon gasification and the two different CO can be clearly distinguished.

The present paper deals with a series of TPD experiments performed in carbon samples with different calcium loadings and obtained after submitting these samples to a chemisorption process with $^{13}\text{CO}_2$ at different temperatures.

EXPERIMENTAL

Samples

The samples used have been extensively described elsewhere [1, 11]. In short, this study concerns with a high purity carbon, obtained from a phenol-phormaldehyde resin oxidized by HNO_3 to create oxygenated surface groups. Calcium is added by means of ionic-exchange or impregnation using a calcium acetate solution. The nomenclature of the samples is the following: A2 (corresponding to the oxidized carbon) followed by I or II, in order to distinguish between impregnation and ionic exchange, and by a number, indicating the amount of calcium loaded.

TPD after $^{13}\text{CO}_2$ interaction. Experimental procedure

The experimental procedure used to obtain the TPD spectra after interaction with $^{13}\text{CO}_2$ consists of the following steps: i) heating of the calcium-carbon sample in He up to 1223 K at 20 K/min heating rate; ii) cooling of the sample in He atmosphere to the treatment temperature (T_i) (i.e. 573 K or 773 K); iii) when the T_i is stabilized, He is switched to Ar; iv) Ar is switched to $^{13}\text{CO}_2$ and the contact with $^{13}\text{CO}_2$ is maintained for 1-1.5 minutes; v) TPD in He (20 K/min) up to 1223 K. The flow rates used were 30 ml/min (25°C, 1 atm).

All data are obtained by MS analysis and all signals are corrected for fragmentation and MS sensitivity.

RESULTS AND DISCUSSION

TPD after $^{13}\text{CO}_2$ interaction

Figure 1 presents the TPD spectra obtained after $^{13}\text{CO}_2$ chemisorption at 573 K on samples A2-II-2.9 and A2-I-1.3; Figure 2 shows the same experiment but after $^{13}\text{CO}_2$ treatment at 773 K on sample A2-I-1.3. In all the TPD runs, the evolution of ^{12}CO , ^{13}CO , $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ with temperature has been followed. The plot of the total CO and CO_2 evolution for the sample A2-II-2.9 (Figure 3) is similar to the TPD spectrum obtained from this sample after $^{12}\text{CO}_2$ chemisorption at 573 K [4], using a different coupled MS-reactor system, which shows the reproducibility of these experiments.

Figures 1 and 2 show that the TPD spectra consist on two $^{13}\text{CO}_2$ peaks and one $^{12}\text{CO}_2$ peak, together with a ^{13}CO peak and a ^{12}CO one. The baseline for the ^{12}CO does not recover the starting value and an increase in the ^{12}CO signal at temperatures higher than 1123 K is observed. This amount released at temperatures higher than 1123 K is independent of the calcium content, as can be deduced from the comparison of the TPD spectra of the samples A2-II-2.9 and A2-I-1.3 (Figure 1). In a previous publication [4] it was pointed out that the CO evolution profile observed at high temperatures corresponds to the decomposition of relatively stable oxygenated surface groups from the carbon itself, which may need temperatures higher than 1300 K for a total decomposition [12, 13]. This interpretation is confirmed by comparing Figures 1 and 2. In fact, the TPD spectrum of Figure 2 has been obtained after that of Figure 1b using the same sample, whereby, the sample has been submitted

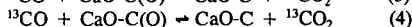
to an additional heat treatment that produces a decrease in the number of surface C(O) complexes evolved at high temperatures.

In spite of the fact that the global TPD spectrum (Figure 3) is similar to the resulting after $^{12}\text{CO}_2$ treatment, it is obvious that the use of $^{13}\text{CO}_2$ allows us to obtain additional information about the calcium-carbon interaction. In this sense: i) three CO_2 peaks (two $^{13}\text{CO}_2$ and one $^{12}\text{CO}_2$) can be distinguished (Figures 1 and 2), whereas a two peak CO_2 profile is observed in Figure 3; ii) two CO peaks are differentiated (one ^{13}CO and one ^{12}CO). This last point constitutes the most relevant aspect of the results of these TPD experiments, because it is in agreement with the two steps mechanism previously proposed from the analysis of TPD runs. These TPD were obtained in He after contacting $^{12}\text{CO}_2$ [4] and from the same kind of experiments but performed under vacuum [9]. This mechanism consists of two steps (reactions (1) and (2)), the ^{13}CO proceeding from the decomposition of active $\text{Ca}^{13}\text{CO}_3$, that is to say, $\text{Ca}^{13}\text{CO}_3$ in the interface of contact with carbon (step (1) of the mechanism) and the ^{12}CO coming from the decomposition of the oxidized carbon sites (CaO-C(O)) of the CaO-carbon interface (step (2) of the mechanism). As this second process constitutes the determining step of the gasification mechanism, the ^{12}CO is released at higher temperatures than the ^{13}CO , as it is observed in Figures 1 and 2.

The interpretation of the different CO_2 peaks that appear in a TPD experiment, requires a more detailed analysis. It seems clear that the first $^{13}\text{CO}_2$ results from the surface or bulk calcium carbonate decomposition (inactive catalyst, which is not in contact with the carbon). This argument is in agreement with previous results [4, 5] in which was observed an increase in the amount of this first CO_2 with calcium loading. This assignment is also confirmed by the shift observed in the peak maximum to higher values with increasing the CO_2 treatment temperature (Figure 1b and 2). When T_1 is higher than 573 K, the bulk calcium carbonate formation starts and hence, the CO_2 uptake increases. During a TPD experiment, this bulk CaCO_3 decomposes partially to the gaseous phase, increasing the CO_2 contribution of the first $^{13}\text{CO}_2$ peak, and shifting the peak temperature to higher values (Figures 1b and 2). It must be emphasized that this reasoning is in apparent contradiction with TPD experiments previously presented [4], obtained in a sample with a 3.7 Ca wt% (A2-I-3.7). In these experiments, the amount of CO_2 related to the first peak remains constant with T_1 , while the total CO evolved increases with T_1 , indicating that the bulk CaCO_3 decomposition is produced mainly through the interface. The discrepancy in the behaviour perhaps is due to the different initial dispersion of the samples studied (0.49 for the A2-I-1.3 and 0.60 for the A2-I-3.7). In any case, a more detailed study is necessary with labelled molecules to make clear this point.

In relation to the two CO_2 peaks ($^{13}\text{CO}_2$ and $^{12}\text{CO}_2$) that appear at temperatures close to the CO ones (^{13}CO and ^{12}CO respectively), the following possibility can be proposed to explain their origin:

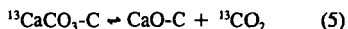
The ^{13}CO , originated from the dissociation of the $\text{Ca}^{13}\text{CO}_3$ of the interface and the ^{12}CO , released during the decomposition of the oxidized carbon sites (CaO-C(O)), can react with oxidized carbon sites while leaving the porous network of the carbon and/or while leaving the CaO-carbon interface. Therefore, some $^{13}\text{CO}_2$ or $^{12}\text{CO}_2$ can be attributed to the following secondary reactions:



However, from the argument proposed we are unable to explain all of the experimental results. In fact: i) TPD experiments performed under high vacuum after CO_2 chemisorption at 573 K [9], show

only two CO_2 peaks whose maxima do not coincide with any of the two CO peaks observed in these experiments; this result indicates that there is some CO_2 that is not produced from secondary and/or parallel reactions. It must be pointed out that under high vacuum conditions, no secondary reactions of CO are observed. ii) The ratio CO/CO_2 calculated from TPD experiments of samples with different calcium sintering degree, decreases with increasing calcium sintering [4, 5]; in this case, should secondary reactions take place, this ratio should be constant. These two results indicate another possibility.

Some $^{13}\text{CO}_2$ of the second peak may also come from $\text{Ca}^{13}\text{CO}_3$ decomposition that is in contact with the carbon. This decomposition is produced without dissociation of the $^{13}\text{CO}_2$ molecule:



Considering these arguments, it is possible to explain the origin of the different CO_2 peaks observed in the TPD experiments obtained after $^{13}\text{CO}_2$ treatment.

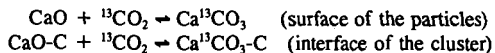
Mechanism of the reaction

From the above results it is possible to confirm the mechanism by which the CO_2 chemisorbed on the CaO reaches, during a TPD experiment, the catalyst-carbon contact and to strengthen the previously proposed mechanism for the carbon-gas reactions catalyzed by calcium [4,5].

$^{13}\text{CO}_2$ contact with the calcium-carbon samples.

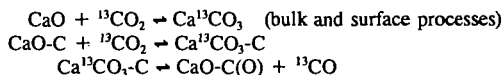
a) $T_i = 573 \text{ K}$

When the calcium-carbon sample, previously heat treated in He up to 1223 K, is contacted with $^{13}\text{CO}_2$ at $T_i = 573 \text{ K}$, the CO_2 interaction is restricted to the CaO molecules on the surface of the particle [2,3]. At this temperature no dissociation of the $^{13}\text{CO}_2$ molecule is found as shown in Figure 4a, in which Ar flow is switched to $^{13}\text{CO}_2$ for 1.5 minutes and then to Ar. Of course when the CaO is highly dispersed, as it occurs in the sample A2-II-2.9 (in which the dispersion degree is 0.56), the catalyst should be as small particles (cluster) where the differentiation between surface and catalyst-carbon interface could not be justified. In any case, particle or cluster, the CO_2 interaction can be presented as:



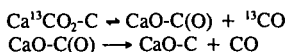
b) $573 \text{ K} < T_i < 823 \text{ K}$.

In this temperature range bulk carbonation occurs [3-5] and, as it is shown in Figure 4b, a small ^{13}CO peak from $\text{Ca}^{13}\text{CO}_3$ decomposition is found. Interestingly, the corresponding ^{12}CO from carbon gasification is not found, indicating the dissociation of the CaO-C(O) species does not take place. Temperatures higher than 823 K are needed to produce the CaO-C(O) complexes evolution, as shown in the TPD experiments of Figures 1 and 2. This type of results are noteworthy because they also allow to distinguish the two types of CO above mentioned. If the dissociation of the $\text{Ca}^{13}\text{CO}_3$ takes place without evolution of ^{12}CO , it is clear that the $^{13}\text{CO}_2$ in this temperature range reaches the interface catalyst-carbon in agreement with previous findings [4,5]. The processes involved are:



c) $T_i > 823 \text{ K}$.

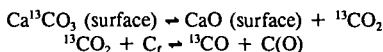
At temperatures higher than 823 K the ${}^{13}\text{CO}_2$ reaches the interface and, because the temperature is high enough, in addition to its dissociation, there is also the gasification of carbon and hence the evolution of the oxygen carbon complexes (CaO-C(O)).



TPD after ${}^{13}\text{CO}_2$ chemisorption at 573 K.

a) During heating in He of a calcium-carbon sample which has been submitted to a chemisorption process in ${}^{13}\text{CO}_2$ at 573 K, the ${}^{13}\text{CO}_2$ previously chemisorbed on the surface of the CaO particle is being redistributed. The ${}^{13}\text{CO}_2$ reaches and occupies the calcium-carbon interface and part remains on the external surface.

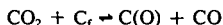
b) As the heating proceeds, the $\text{Ca}^{13}\text{CO}_3$ on the surface of the particle (which is not in contact with the carbon), decomposes giving ${}^{13}\text{CO}_2$. Part of this ${}^{13}\text{CO}_2$ may interact with active carbon sites producing oxidized carbon atoms C(O) and ${}^{13}\text{CO}$. It could be observed in Figures 1 and 2 that parallel to the appearance of the ${}^{13}\text{CO}_2$ there is also a shoulder in the ${}^{13}\text{CO}$ peak.



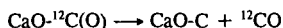
c) At higher temperatures the active CaCO_3 in the catalyst-carbon contact, which could form an intermediate $\text{CaO} \cdot \text{CO}_2\text{-C}$, decomposes giving:



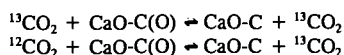
Most of the ${}^{13}\text{CO}$ peak of the Figures 1 and 2 comes from this reaction. Using TPD experiments in vacuum [9], it has been observed that this process is strongly affected by pressure (a shift of $\approx 100 \text{ K}$ in the peak temperature is observed), indicating that this step is mainly in equilibrium. This fact is in agreement with the first step of the widely accepted mechanism of the carbon-gas reaction [14-16].



d) At higher temperatures (as shown in Figures 1 and 2) the decomposition of the oxidized carbon atoms in contact with the catalyst takes place, giving rise to the ${}^{12}\text{CO}$ peak.



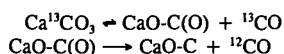
e) Both the ${}^{13}\text{CO}_2$ and the ${}^{12}\text{CO}_2$ produced may also be ascribed to a secondary and/or parallel reactions between the large number of ${}^{13}\text{CO}$ released and oxidized carbon atoms.



f) Part of the CaCO_3 in contact with the carbon (maybe the perimeter of the contact zone) decomposes at slightly higher temperatures giving rise to part of the second ${}^{13}\text{CO}_2$ peak of Figures 1 and 2, which is superimposed with the ${}^{13}\text{CO}_2$ formed from the secondary and/or parallel reactions (point e). The CO_2 released as a consequence of this decomposition is clearly distinguished in the TPD experiments performed under vacuum [9].

CONCLUSIONS

TPD experiments performed in carbon samples with different calcium loadings which were previously contacted with ${}^{13}\text{CO}_2$ at 573 K and 773 K, have allowed to distinguish clearly two types of CO produced: ${}^{13}\text{CO}$ as a consequence of the dissociation of the CO_2 coming from active CaCO_3 decomposition at the catalyst-carbon contact- and ${}^{12}\text{CO}$ coming from carbon gasification -via decomposition of the oxidized carbon sites-. These two CO peaks of similar intensities confirm the following steps of the mechanism of the CO_2 gasification of carbon catalyzed by calcium:



ACKNOWLEDGEMENTS

The authors thanks to the DIGCYT (project PB-88-0295), to the MEC for Diego Cazorla's Thesis grant and to the Department of Chemical Engineering of the University of Amsterdam.

REFERENCES

1. C. Salinas-Martínez de Lecea, M. Almela-Alarcón and A. Linares-Solano, *Fuel*, **69**, 21, (1990).
2. A. Linares-Solano, M. Almela-Alarcón and C. Salinas-Martínez de Lecea, *J. Catal.*, **125**, 401, (1990).
3. D. Cazorla-Amorós, J.P. Joly, A. Linares-Solano, A. Marcilla-Gomis and C. Salinas-Martínez de Lecea, Accepted in *J. Phys. Chem.*
4. D. Cazorla-Amorós, A. Linares-Solano, C. Salinas-Martínez de Lecea and J.P. Joly, *Carbon*, **29**, 361, (1991).
5. A. Linares-Solano, C. Salinas-Martínez de Lecea, D. Cazorla-Amorós and J.P. Joly, *Fundamental Issues in Control of Carbon Gasification Reactivity*, (Eds. J. Lahaye and P. Ehrburger), NATO ASI Series E192, p. 409, Kluwer Academic Publishers, 1991.
6. D. Cazorla-Amorós, C. Salinas-Martínez de Lecea, A. Linares-Solano and A. Marcilla-Gomis, *International Symposium on Carbon, New Processing and New Applications*, Tsukuba, Tanso, Vol. 1, 4-8 Nov., p. 356, (1990).
7. D. Cazorla-Amorós, A. Linares-Solano, A.F. Marcilla-Gomis and C. Salinas-Martínez de Lecea, submitted to *Energy & Fuels*.
8. R. Meijer, M. Weeda, F. Kapteijn and J.A. Moulijn, Accepted in *Carbon*.
9. D. Cazorla-Amorós, A. Linares-Solano, C. Salinas-Martínez de Lecea, T. Kyotani, H. Yamashita and A. Tomita, in preparation.
10. F. Kapteijn, R. Meijer, B. van Eck and J.A. Moulijn, *Fundamental Issues in Control of Carbon Gasification Reactivity*, (Eds. J. Lahaye and P. Ehrburger), NATO ASI Series E192, 221,

- Kluwer Academic Publishers, 1991.
11. A. Linares-Solano, M. Almela-Alarcón, C. Salinas-Martínez de Lecea, Am. Chem. Soc. Division of Fuel Chemistry, **34**(1), 136, (1989).
 12. J. Wang, B. McEnaney, XIX Biennial Conference on carbon, Pennsylvania, U.S.A., p. 590, (1989).
 13. B. McEnaney, Fundamental Issues in Control of Carbon Gasification Reactivity, (Eds. J. Lahaye and P. Ehrburger), NATO ASI Series E192, 175, Kluwer Academic Publishers, 1991.
 14. F. Kapteijn and J.A. Moulijn, Carbon and Coal Gasification, (Eds. J.L. Figueiredo and J.A. Moulijn), NATO ASI Series E 105, 291, Martinus Nijhoff, 1986.
 15. H. Freund, Fuel, **64**, 657, 1985.
 16. H.J. Mühlen, K.H. van Heek and H. Jüntgen, Fuel, **64**, 994, (1985).

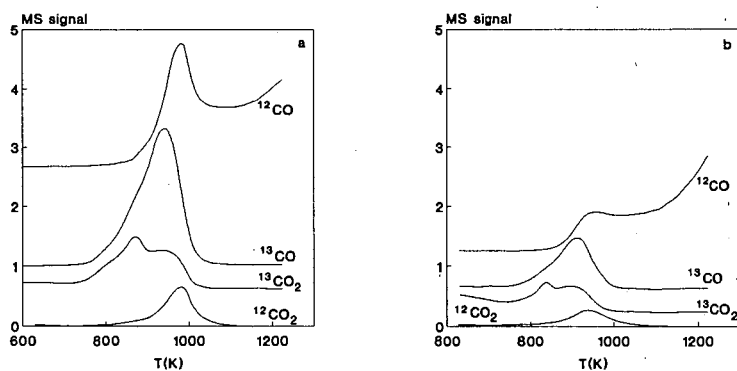


Figure 1. TPD-MS spectra obtained after $^{13}\text{CO}_2$ chemisorption at 573 K on samples: a) A2-II-2.9 and b) A2-I-1.3.

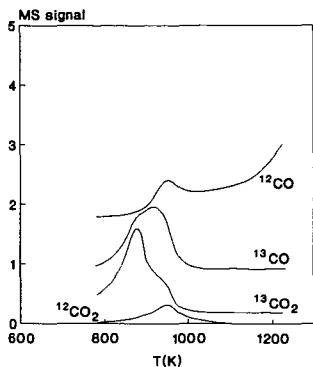


Figure 2. TPD-MS spectrum obtained after $^{13}\text{CO}_2$ treatment at 773 K on sample A2-I-1.3.

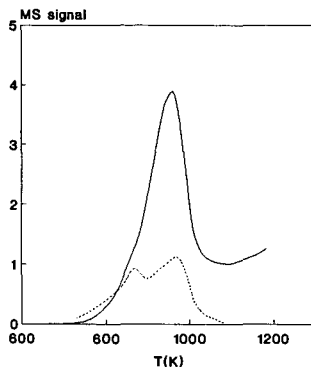


Figure 3. Total CO and CO_2 evolutions after $^{13}\text{CO}_2$ chemisorption at 573 K on sample A2-II-2.9 (—, CO; ---, CO_2).

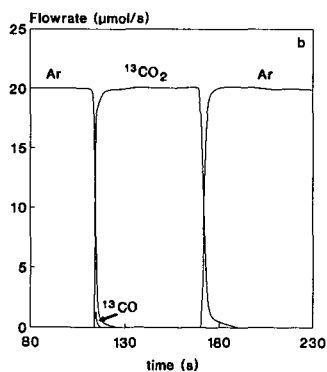
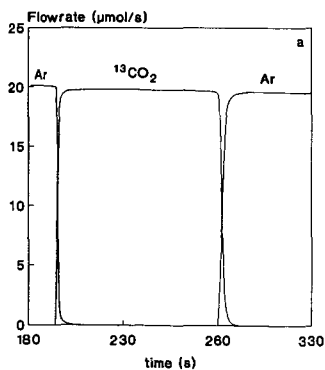


Figure 4. a) $^{13}\text{CO}_2$ chemisorption at 573 K on sample A2-II-2.9; b) $^{13}\text{CO}_2$ chemisorption at 773 K on sample A2-II-2.9.